TECHNOLOGY DEPARTMENT

PREPARATION OF TANTALUM-COLUMBIUM ALLOY POWDERS

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ABSTRACT

Techniques were studied for the preparation of homogeneous columbium-tantalum alloy powders. A powder metallurgy approach was found satisfactory. Quantities of -200 mesh powder ranging from 4.2 to 4.7 pounds were prepared for each of the following nominal compositions: 25% tantalum-75% columbium, 50% tantalum-50% columbium, 75% tantalum-25% columbium, and 100% tantalum. Final nitrogen content was somewhat higher than desired, but the powders were satisfactory in other respects.

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A. Introduction

The Metals Research Laboratories acted as a sub-contractor, under Kemet P. O. 233-41344, for contract No. NObsr-87478 between the Navy Bureau of Ships and Kemet Department of the Linde Company. The objective of the sub-contract effort was to prepare and analyze several pounds each of four different alloy powders, 25% tantalum-75% columbium, 50% tantalum-50% columbium, 75% tantalum-25% columbium, and 100% tantalum. The powders were to be submitted to the prime contractor for evaluation.

The contractor preferred that the alloys be prepared by powder metallurgy techniques. This necessitates homogenization of the alloy composition during the sintering operation. Estimates of interdiffusion coefficients in the tantalum-columbium alloy system, as described in the Appendix, indicated that homogeneity could be achieved by sintering for several hours at a temperature of 2000°C. or higher with well blended, -200 mesh powders. Accordingly, the powder metallurgy approach appeared to be feasible.

The experimental program consisted of first piloting small samples of two compositions to determine whether a satisfactory product could be obtained and subsequently proceeding with the preparation of several pounds of each composition. Because of time considerations, the two phases overlapped and production of the final powder was initiated as soon as it was indicated that homogeneity could be achieved with the first of the two pilot samples.

B. Experimental Techniques

Two ball mills, each of about one-gallon capacity, were used for milling and blending. One mill was lined with tantalum and utilized arc-cast tantalum buttons as grinding media while the other was lined with columbium and utilized rectangular lumps of columbium plate trimmings. Both mills were equipped with O-ring seals and were loaded and unloaded in an argon-filled dry box. Either vibratory or rotating milling action was used.

Compacting was done in a piston-type hydrostatic press having a 1.77-inch diameter chamber with glycerin as the fluid media. Load was applied to the piston via a 500-ton hydraulic press.

Heat-treatment was done in an NRC resistance-heated vacuum furnace, type 2915B, equipped with tungsten heating elements and tungsten-molybdenum heat shields. The furnace is designed to operate for prolonged periods at 2200°C. and intermittently at temperatures up to 2400°C. in vacuum, inert gas, or hydrogen atmospheres. When hydrogen was used, cylinder hydrogen was passed through a platinum catalyst and a Lectrodryer to provide a dew point of about -40°C. Temperature was measured with an optical pyrometer. The furnace does not provide perfect blackbody conditions, so corrections must be made for emittance, and the furnace manufacturer provided temperature corrections for the range of 1600 to 2150°C. The correction was approximately 100°C. for the sintering range used in this program.

Arc melting for control samples was accomplished in a tungsten electrode furnace equipped with water-cooled copper hearth plates. Melting was done in an atmosphere of helium, pre-purified by passing through zirconium chips heated to 800°C. A columbium button was melted first to further getter the atmosphere.

Homogeneity was studied by means of an AEI electron microprobe. The spot diameter was approximately 2 microns and radiation was measured for 40 seconds.

Density was determined by displacement in mercury.

C. Preparation of Pilot Alloys

1. 25% Tantalum Alloy

The 25% tantalum composition was selected for the initial processing study since this alloy had the lowest interdiffusion coefficient. The alloy was processed in accordance with the flowsheet shown in Figure 1. It was considered appropriate to include an arc-melting step in the initial study as a control and in the event that an alternative consolidation technique would be required.

a. Milling

Hydrogen-bearing columbium from Lot BM 818 and hydrogen-bearing tantalum from Lot 1883 were ball milled to -200 mesh in the columbium-lined and tantalum-lined mills, respectively. A 3/4-pound charge of tantalum was completely reduced to -200 mesh in one hour whereas a 2-pound charge of columbium was 78% reduced to -200 mesh in 6.5 hours. The relative ease of milling of the two materials is undoubtedly largely due to their respective hydrogen contents. Particle size distribution is shown in Figure 2, and interstitial content before and after milling in Table I. Both the oxygen and carbon contents increased during milling. The hydrogen contents shown in Figure 2 are for the as-milled material. The particle size distribution was determined after dehydriding, but the distribution should not be affected significantly by that treatment.

b. Dehydriding

The tantalum powder was dehydrided by slowly heating to the temperature range of 700 to 800°C. in vacuum and holding until degassing was complete The final furnace pressure was 0.06 micron and the leak rate cold was 0.36 micron per hour. The columbium powder was dehydrided in the same manner. The final pressure was less than 0.01 micron and the leak rate was 1.8 microns per hour. The dehydriding treatment had no significant effect on the bulk density but the oxygen content was apparently increased by about 8% as shown in Table I.

c. Blending

A charge of 200 g. tantalum and 600 g. columbium was blended in the columbium-lined ball mill for 30 minutes and rescreened through 200 mesh. The bulk density is given in Table I.

d. Compacting

An attempt was made to press a one-pound compact 1/2 inch wide by 10

inches long in unlubricated steel dies at 35 TSI. This was not satisfactory as the compact had poor green strength and crumbled during handling.

Subsequently, five samples weighing from 11 to 188 g. each (a total of 409 g.) were compacted hydrostatically at 40 TSI in cylindrical plastisol molds, 1/2 to 7/8 inch in diameter. The resulting compacts had a green density of 8.0 g./cm.^{3} and the green strength was quite satisfactory.

e. Sintering

The compacts were sintered in a tantalum crucible containing a bed of blended 25% tantalum-75% columbium alloy powder. The sintering conditions were as follows:

Temperature, °C.			Time Hr.	Final Pressure Micron
Optical		Estimated		
Range	Nominal	True		
1970-2050	2025	2120	.23	0.02

The loose powder sintered to the crucible and to the compacts and was not recovered. The compacts were successfully broken out with a small amount of sintered powder adhering to the bottom of each compact. Chemical analysis indicated a marked reduction in interstitial content during sintering as shown in Table I. The sintered density was 9.3 g./cm.^{3}.

f. Arc Melting

Three of the sintered bars weighing a total of 211 g. were tungsten arc melted four times in 1/2- by 1- by 5-inch copper bar mold, inverting between each melt. The current was 300 to 480 amp. DCSP. Analysis indicated a further reduction in carbon content and a slight increase in oxygen content (Table I). Density increased to 10.1 g./cm.^{3}.

g. Homogeneity

Transverse sections 1/4 inch thick were cut from the center of the arc-melted bar and from a sintered bar. Metallographic examination revealed no gross inhomogeneity. The sintered bar contained numerous small pores rather uniformly distributed while the arc-melted bar was free from porosity as would be anticipated by the high density.

The results of electron microprobe examination are given in Table II. The reported values for tantalum were calculated from a pure tantalum standard and may not be quantitatively precise, but the relative tantalum content among the various spots in the same sample should be quite precise. A new filament was installed in the probe prior to examination of the arc-melted sample. Filaments tend to be somewhat unstable until aged and several readings were discarded because of an obvious drift in filament current. This tendency toward instability may account for the slightly larger standard deviation in that sample. However, the homogeneity of both samples appeared to be quite satisfactory for this investigation in which the nominal gross alloy content differs by 25% between compositions.

The average tantalum content of the arc-melted sample was 8% higher than that of the sintered sample. No great significance should be attached to this in the absence of confirming quantitative analysis since the calibration would be affected by surface condition of the specimen and density of the spot volume. The density difference between the two samples is in the right direction to account for the difference in apparent average tantalum content.

h. Hydriding

Tantalum absorbs hydrogen quite rapidly at temperatures in the order of 400 to 500°C.(1). The critical temperature range for columbium is probably quite close to that for tantalum. With large masses of metal, hydriding is usually accomplished by heating the charge above the critical temperature then allowing it to cool within the furnace. The cooling rate through the critical range is sufficiently slow so that ample quantities of hydrogen are absorbed, provided that the surface of the metal is clean. Since the mass of the charge in the present program was so small, the cooling rate through the critical range was controlled by reducing the furnace current periodically. The critical temperature was below the range at which the optical pyrometer could be used, so it was necessary to step cool in small current increments and to define the critical range by observing a drop in the hydrogen pressure. The furnace was then maintained at constant current until the pressure became stable. In order to provide a greater surface area for absorption, the sintered and arc-melted bars were cold-rolled to a maximum of 1/16-inch thick sheet which was degreased and pickled in 10% HF-90% HNO_3. The sheet was sheared into small pieces and placed in tungsten crucibles for the hydriding operation.

The first three attempts at hydriding were unsuccessful due to leaks developing in the vacuum furnace during the run and/or cooling too rapidly through the critical range. On the fourth attempt, a technique was adopted which appeared to be satisfactory. The charge was heated to 1400°C. in vacuum to distill off any surface impurities and dissolve any residual oxide film. Hydrogen was then introduced to one-pound positive pressure and the furnace allowed to cool to 700 to 800°C. Thereafter the furnace current was reduced in 50-ampere steps (corresponding to 30 to 50°C) every 30 minutes until a distinct pressure drop was noted. Thereafter, the furnace was held at each current increment until hydrogen absorption appeared to be complete. When no pressure drops were observed during further step cooling, the power was shut off and the furnace cooled overnight under one-pound hydrogen pressure. The hydrogen content of the alloy was increased to 870 parts per million and the sheet was embrittled.

i. Milling

The hydrided sheet was ball milled in a columbium-lined mill and 71% of the charge was reduced to -200 mesh in eight hours. The powder was not further analyzed as furnace leaks were known to have developed during two of the hydriding runs and the product would not be expected to have high purity.

2. 75% Tantalum Alloy

It was thought advisable to prepare a small sintered bar of the 75% tantalum composition for homogeneity determination, to ensure that there was no

(1) G. L. Miller, Metallurgy of the Rarer Metals, 6, Niobium and Tantalum, Academic Press, Inc., New York (1959)

adverse and unexpected effect of composition on the sintering characteristics. The techniques were the same as those used for the 25% tantalum alloy.

The first 100-g. charge was lost during blending when a holding strap on the vibratory ball mill broke and the contents were thrown out of the mill. A second 100-g. charge was lost when a ceramic boat was inadvertently used as a support for the compact during sintering. The ceramic melted and contaminated the compact. An additional 102 g. were absorbed in the columbium lining of the ball mill during blending, but a 98-g. compact was successfully prepared and sintered in a tantalum crucible under the following conditions:

Temperature, °C.			Time Hr.	Final Pressure, Micron
Optical		Estimated		
Range	Nominal	True		
2050-2150	2100	2205	23.5	< 0.01

The interstitial content was effectively reduced during sintering and the density was increased to 12.8 g./cm.^{3} as shown in Table I.

The results of electron microprobe examination of a sample cut from the center of the bar are included in Table II. The homogeneity was comparable to that achieved with the 25% tantalum alloy.

No further work was done with the 75% tantalum pilot alloy sample.

D. Preparation of Production Alloys

The pilot program indicated that satisfactory homogeneity could be achieved by the powder metallurgy route. Consideration of various losses suggested that an 80% recovery might be expected. Since the target quantity was five pounds of each composition, an initial charge of 2840 g. per alloy was used. The alloys were produced in accordance with the flowsheet shown in Figure 3.

1. Milling

The columbium and tantalum were taken from the same lots as were used for the pilot alloys. The columbium was not sufficiently brittle for milling to -200 mesh in the quantities required for the production alloys, as only 1/2 pound of -200 mesh was obtained after six hours milling of a 9-pound charge and only 1 pound was obtained after 7-3/4 hours milling of a 4-1/2-pound charge. Therefore, the columbium was rehydrided in the same furnace run as the final hydriding operation with the 25% tantalum pilot alloy. The resulting hydrogen content was 0.85%, and 100% of that material was milled to -200 mesh in six hours. The particle size distribution shown in Figure 2 indicated a smaller proportion of the coarser fractions (> 25 microns) than had been obtained with the material used for the pilot alloys.

The tantalum milled satisfactorily without rehydriding. The size distribution was slightly altered from that prepared for the pilot alloy (Figure 2), probably because of the increased charge weight and increased milling time.

2. Dehydriding

The tantalum was dehydrided by heating overnight in vacuum at a maximum temperature of 975°C. The final pressure was 0.01 micron. The columbium was

dehydrided in the same manner at a maximum temperature of 845°C. with a final pressure of 0.04 micron.

3. Blending

The alloy additions were weighed and blended for 30 minutes in the tantalum-lined ball mill. An appreciable weight gain was obtained in each case. This was assumed to be tantalum pickup from the mill lining and the tantalum grinding media which would alter the nominal alloy tantalum content as shown in Table III. The interstitial analyses included in Table III will be discussed in a later section.

4. Compacting

Cylindrical compacts were prepared by hydrostatic pressing in rubber molds at 40 TSI. The green compacts were 3/4 to 1 inch in diameter by 1 to 1-1/2 inches high and weighed 145 to 165 g. Green densities are given in Table III.

5. Sintering

The compacts were stacked on a tungsten plate for sintering under the conditions given in Table IV. The intent was to sinter two alloys at one time but it was found too difficult to keep the charge from contacting the heating elements with such a large mass in the furnace. After the first run, a single alloy was sintered at one time. One attempt was made to hydride during cooling from the sintering cycle but insufficient hydrogen was absorbed, presumably due to the low surface area:volume ratio of the compacts.

For these prolonged heat-treatments, the furnace was allowed to run unattended overnight since it was equipped with safety devices which would prevent damage due to power failure, low water pressure, leaks in the vacuum chamber, etc. On several occasions, the furnace shut off during the night, causing some uncertainty in the sintering time for two of the alloys. However, all materials except the unalloyed tantalum were sintered for at least 24 hours. Since no interdiffusion was required for the tantalum, the minimum of 18 hours was considered adequate.

A total of nine furnace runs were required to complete sintering of the four alloys. The tungsten heating elements were replaced three times, twice because the elements warped and cracked upon contacting the charge, and once when they were broken in handling while a leak was being repaired at the bottom of the furnace.

6. Cold-Rolling

All compacts were cold-rolled to 0.037-inch thick sheet, degreased, and pickled in 10% HF-90% HNO_3 prior to hydriding. The density of the cold-rolled material closely approached theoretical density as indicated in Figure 4. Theoretical density was estimated to vary linearly with the atomic per cent of tantalum present.

7. Hydriding

Hydriding was done in accordance with the technique devised for the pilot alloy. A typical furnace record is shown in Figure 5. The relatively

large-mass of the charge in hydriding the production alloys resulted in a lower cooling rate after the power was shut off. Consequently, hydrogen contents of these alloys were much higher than that of the pilot alloy, ranging from 2800 to 5900 p.p.m. (Table III).

8. Milling

The 25% tantalum alloy was milled in the columbium-lined ball mill and all others in the tantalum-lined mill. Milling loss varied between 70 and 482 g. Recovery figures are given in Table V, including the overall values for the production operation.

9. Product Analysis

A riffled sample of the -200 mesh powder was analyzed for particle size distribution, bulk density, and chemistry. Bulk density increased with tantalum content as shown in Table III and Figure 4. Particle size distribution is shown in Figure 6. The 26% tantalum alloy contained the least fines despite the highest hydrogen content and the longest milling time. The unalloyed tantalum contained the greatest amount of -400 mesh material.

Chemical analyses are given in Table III and the estimated change in purity from the starting material is shown below:

Element	Alloy			
	25 Ta	50 Ta	75 Ta	100 Ta
C, p.p.m.	-25	-120	-85	-70
O, p.p.m.	-450	-900	-1450	-700
N, p.p.m.	+78	+275	+542	+270
Ta, %	+1.3	+7.3	+5.8	-1.0*
Accountable Ta, %	1.3	1.8	2.0	0
Unaccountable Ta, %	0	5.5	3.8	1.0

* Based on Cb pickup of 1%

The carbon and oxygen contents were reduced during processing but the nitrogen content increased. The elemental columbium starting material had an abnormally high nitrogen content of 630 p.p.m., an increase of 500 p.p.m. over the lot analysis. This was unexpected and since the analysis was not available until after blending and compacting had been completed and sintering was partially completed, it was not possible to make substitution at that time. Data for the two pilot alloys indicated that nitrogen would be reduced during the sintering step so it was anticipated that the final nitrogen contents of the production alloys would be low despite the relatively high initial nitrogen content. However, nitrogen increased rather than decreased during processing. Nitrogen could be introduced into the process through an undetected leak in the vacuum furnace, as an impurity in the hydrogen gas, or possibly during milling. The actual source of the nitrogen is not known at this time. The only known source for tantalum pickup would be the ball mill used for blending and milling. The weight gain during blending could account for that portion of the increase labeled "accountable tantalum." The additional tantalum in the 50 and 75% tantalum alloys could result from a net gain in tantalum during the final milling operation despite the overall weight loss or from a combined alloy loss and tantalum pickup during the blending operation. The former reason is favored since the 25% tantalum alloy was milled

in a columbium-lined mill and contained no unaccountable tantalum. Any tantalum picked up during the final milling operation would be present as elemental tantalum and would be presumably distributed uniformly throughout the alloy powder.

The 1% columbium in the unalloyed tantalum powder was undoubtedly picked up from the ball mill.

E. Materials Balance

A materials balance for the raw materials, pilot alloys, and production alloys is presented in Tables VI, VII, and VIII, respectively.

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TABLE I

Density and Composition of Pilot Alloys

Density, g./cm.^{3}		Unalloyed Columbium	Nominal 25% Ta	Nominal 75% Ta	Unalloyed Tantalum
Bulk, -200 mesh, hydrided*		3.6	-	-	6.6
Bulk, -200 mesh, dehydrided*		3.5	4.1	5.6	6.6
Green, 40 TSI compact		-	8.0	10.4	-
Sintered		-	9.3	12.8	-
Sintered and arc melted		-	10.1	-	-
Bulk, alloyed powder*		-	3.8	-	-
Composition, p.p.m.					
As-received, Lot analysis	C	80	-	-	160
	O	2700	-	-	2000
	N	130	-	-	90
-200 mesh, as-milled	C	220	-	-	590
	O	3800	-	-	2700
	H	1500	-	-	3500
-200 mesh, dehydrided**	C	250	(338)	(512)	600
	O	4100	(3800)	(3200)	2900
	H	< 10	(< 10)	(< 13)	< 13
	N	190	(172)	(138)	120
Sintered	C	-	150	60	-
	O	-	200	300	-
	H	-	< 10	17	-
	N	-	< 100	< 100	-
Sintered and arc melted	C	-	50	-	-
	O	-	300	-	-
	H	-	12	-	-
	N	-	< 100	-	-
-200 mesh, hydrided alloy powder	H	-	870	-	-

* Converted from Scott density, g./in.^{3}

** Alloy interstitial content calculated from that of elemental additions

TABLE II

Electron Microprobe Analysis of Pilot Alloys

25% Ta-75% Cb						75% Ta-25% Cb		
Sintered			Arc Melted			Sintered		
Location	No.	% Ta	Location	No.	% Ta	Location	No.	% Ta
Random spots on unetched surface	1	26.1	Random spots on unetched surface	1	29.0	Longitudinal survey, spots spaced 500-600 microns on unetched surface	1	76.8
	2	23.8		2	29.9		2	79.0
	3	27.0		3	27.1		3	76.8
	4	26.7		4	27.7		4	78.1
	5	26.7		5	29.2		5	76.3
	6	26.4		6	27.5		6	74.5
	7	27.1		7	28.5		7	75.3
				8	29.9		8	77.2
Etched, Grain 1	8	26.2					9	76.7
" "	9	26.4	Etched, Grain 1	9	26.8		10	78.8
" "	10	26.8	" "	10	26.8			
Etched, Grain 2	11	26.2	" "	11	26.9	Transverse survey, as above	11	78.2
" "	12	25.9	Etched, Grain 2	12	28.8		12	79.8
" "	13	26.0	" "	13	28.0		13	75.1
Etched, Grain 3	14	25.6	" "	14	28.0		14	75.2
			Etched, Grain 3	15	29.5		15	75.0
			Etched, G. boundary	16	29.5		16	77.2
							17	76.8
							18	75.9
							19	75.3
							20	77.2

Statistical Analysis

Sample	No. of Determinations	% Tantalum Avg.	High	Low	Range	Std. Dev.
25% Ta, sintered	14	26.2	27.1	23.8	3.3	0.78
25% Ta, arc melted	16	28.3	29.9	26.3	3.6	1.04
75% Ta, sintered	20	76.8	79.8	74.5	5.3	1.44

TABLE III

Density and Composition of Production Alloys

Density, g./cm.^{3}		Unalloyed Columbium	Nominal 25% Ta	Nominal 50% Ta	Nominal 75% Ta	Unalloyed Tantalum
Bulk, blended powder*		3.1	4.2	5.3	6.1	6.2
Green, 40 TSI compact		-	8.0	9.2	11.0	12.8
Sintered and cold-rolled		-	9.8	10.7	13.3	16.4
Bulk, alloyed powder*		-	3.7	4.4	5.4	6.6
Composition, p.p.m.						
-200 mesh, dehydrided blended powder**	C	100	(125)	(150)	(175)	200
	O	4500	(4050)	(3600)	(3150)	2700
	H	16	(80)	(143)	(206)	270
	N	630	(502)	(375)	(248)	120
	Ta (%)	-	(26.3)	(51.8)	(77.0)	Bal.
-200 mesh, hydrided alloy powder	C	-	100	30	90	130
	O	-	3600	2700	1700	2000
	H	-	5900	5100	3200	2800
	N	-	580	650	790	390
	Ta (%)	-	26.3	57.3	80.8	Bal.
	Cb (%)	-	72.2	41.4	18.3	0.96

* Converted from Scott density, g./in.^{3}

** Alloy interstitial content calculated from that of elemental additions; alloy tantalum content corrected for weight gain during blending.

TABLE IV

Sintering Conditions for Production Alloys

Alloy	Temperature, °C. Optical Range	Optical Nominal	Estimated True	Time, Hr.	Final Pressure, Micron
25Ta-75Cb	2025-2060	2050	2150	24	< 0.01
50Ta-50Cb	2020-2070	2050	2150	24	0.04
75Ta-25Cb	1970-2100	2050	2150	26.5*	0.02
100Ta	2020-2130	2050	2150	18 *	0.02

* Minimum

TABLE V

Recovery Values for Production Alloys

Alloy	Recovery of -200 Mesh Powder: Final Milling % of Charge	Final Milling % of Product	Overall % of Charge	Overall % of Blend
25% Ta	76	94	67	66
50% Ta	78	84	72	69
75% Ta	72	82	73	68
100% Ta	81	87	75	75

TABLE VI

Materials Balance for Raw Materials
(Weight Given in Grams)

	Columbium		Tantalum	
Purchased	5448		9420	
Net gain during milling	188		0	
Total	5636	5636	9420	9420
Alloy Uses				
25% Ta pilot alloy	800		200	
75% Ta pilot alloy	50		283	
75% Ta production alloy	710		2130	
50% Ta production alloy	1420		1420	
25% Ta production alloy	2130		710	
100% Ta production alloy	0		2840	
Subtotal	5110	5110	7583	7583
Losses				
Milling	0		546	
Dehydriding, sampling, misc.	209		203	
Subtotal	209	209	749	749
On Hand				
-200 Mesh	45		372	
+200 Mesh	272		716	
Subtotal	317	317	1088	1088
Total		5636		9420

TABLE VII

Materials Balance for Pilot Alloys
(Weight Given in Grams)

Raw Materials	25% Ta-75% Cb		75% Ta-25% Cb	
Columbium, -200 mesh	600		50	
Tantalum, -200 mesh	200		283	
Blended 25Ta-75Cb, -200 mesh	—		67	
Total	800	800	400	400
Losses				
Blending and compacting	50		203	
Sintering	145		105	
Cold-rolling and pickling	13		-	
Hydriding and milling	84		-	
Sampling and misc.	39		-	
Charge for 75Ta-25Cb alloy	67		28	
Subtotal	398	398	336	336
On Hand				
Blended powder	129		-	
Sintered bar	-		64	
Sintered powder, hydrided				
-200 mesh	191		-	
+200 mesh (scrap)	82		-	
Subtotal	402	402	64	64
Total		800		400

TABLE VIII

Materials Balance for Production Alloys
(Weight Given in Grams)

Item	25Ta-75Cb		50Ta-50Cb		75Ta-25Cb		100Ta	
	Δ W	Bal.	Δ W	Bal.	Δ W	Bal.	Δ W	Bal.
Cb, -200 mesh, dehydrided	+2130	2130	+1420	1420	+710	710	0	0
Ta, -200 mesh, dehydrided	+710	2840	+1420	2840	+2130	2840	+2840	2840
Blended, Ta-lined mill*	+50	2890	+110	2950	+249	3089	Not done	2840
Compacted, hydrostatic, 40 TSI	-65	2825	-72	2878	-22	3067	-39	2801
Sintered, cold-rolled, pickled	-215	2610	-158	2720	-117	2950	-101	2700
Hydrided	-70	2540	-80	2640	0	2950	-40	2660
Ball milled, Ta-lined mill**	-482	2058	-162	2478	-349	2601	-70	2590
Sampled (-200 mesh)	-28	2030	-27	2451	-32	2569	-30	2560
Product on Hand								
-200 mesh	+1910	1910	+2039	2039	+2086	2086	+2130	2130
+200 mesh ***	+120	2030	+412	2451	+483	2569	+430	2560

* Weight gain assumed to be Ta from the balls and lining
** Cb-lined mill used for 25Ta-75Cb alloy
*** Includes some material from balls and mill lining

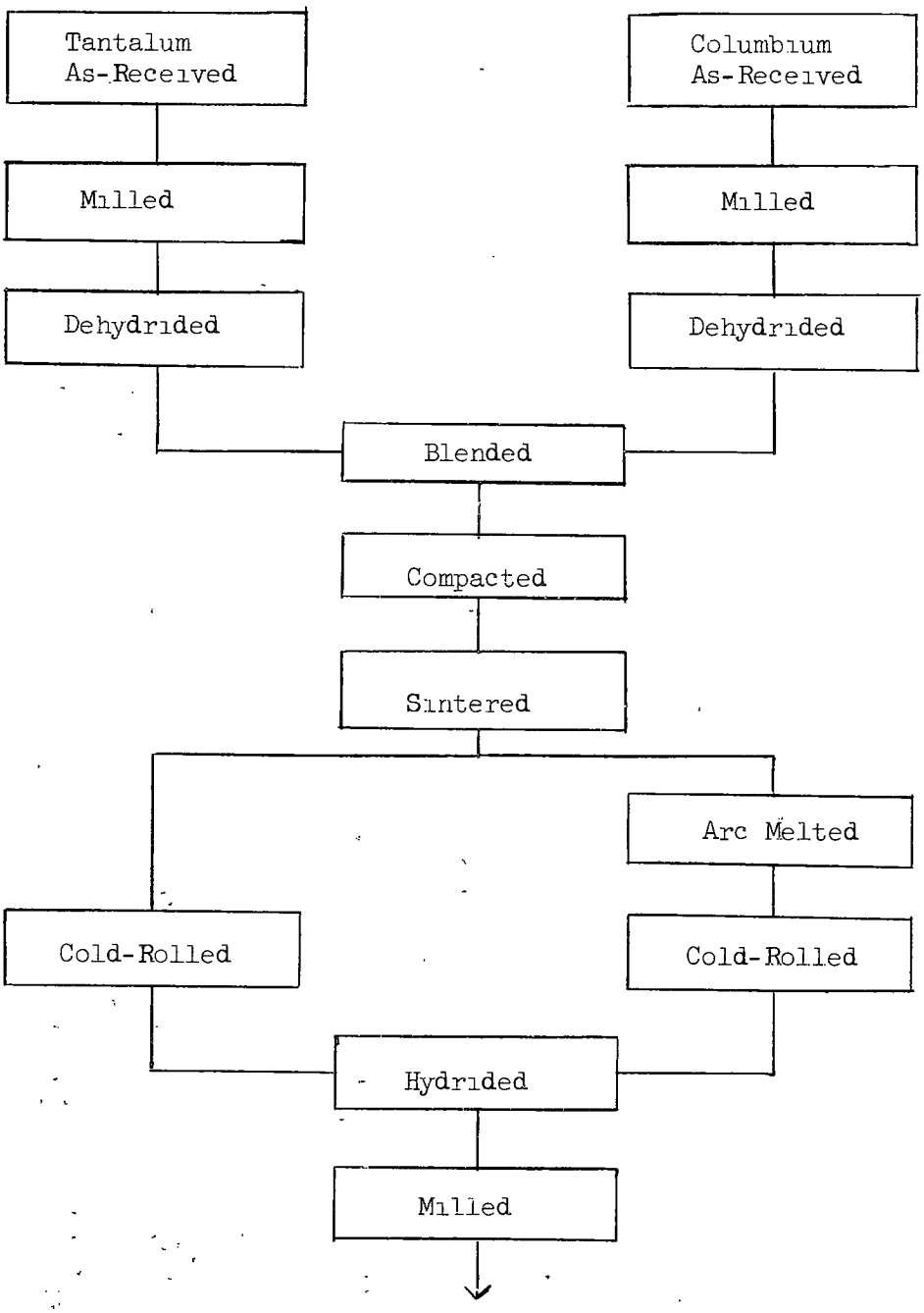

FIGURE 1 - Flowsheet for 25% Tantalum-75% Columbium Pilot Alloy

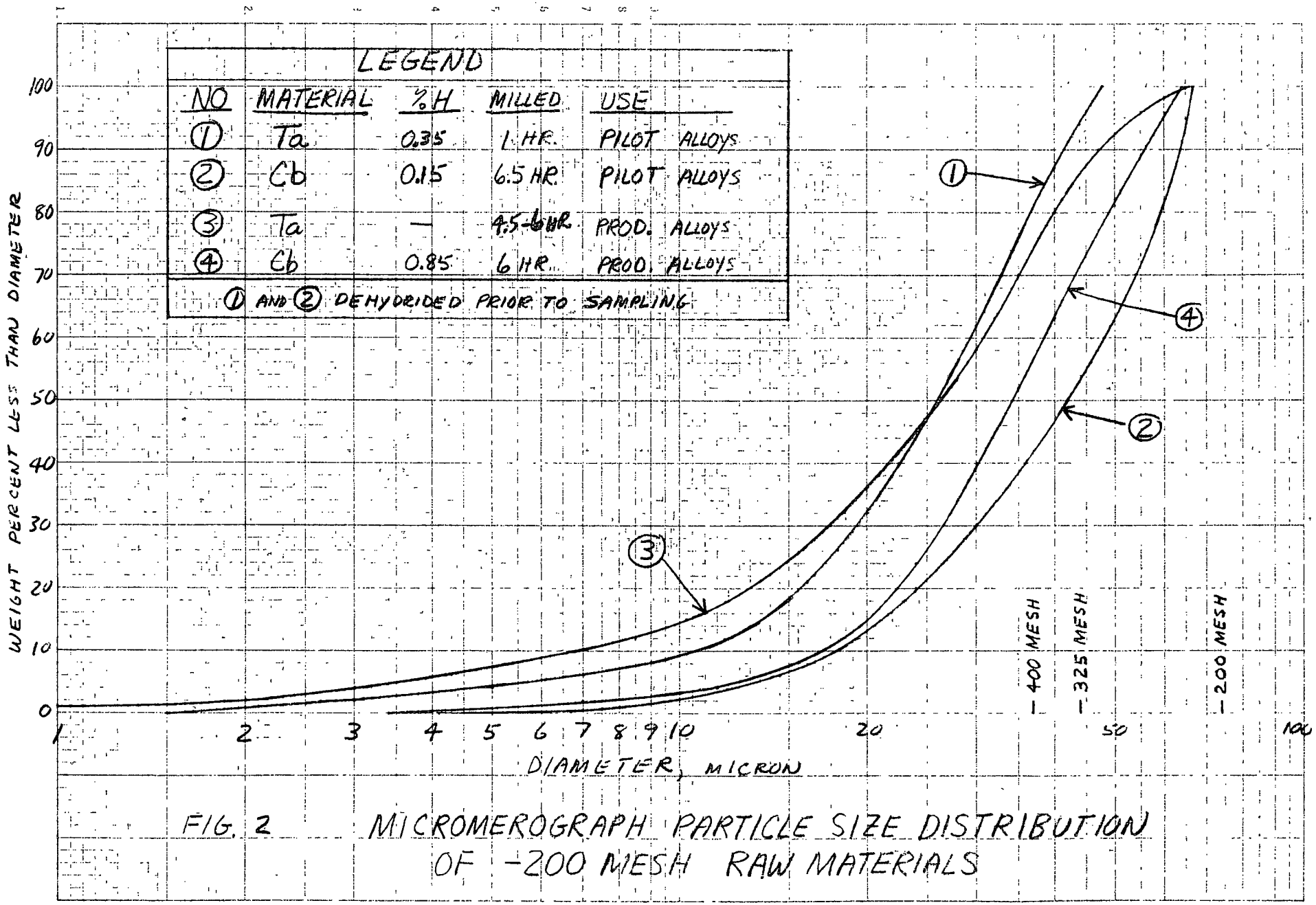

FIG. 2 MICROMEROGRAPH PARTICLE SIZE DISTRIBUTION OF -200 MESH RAW MATERIALS

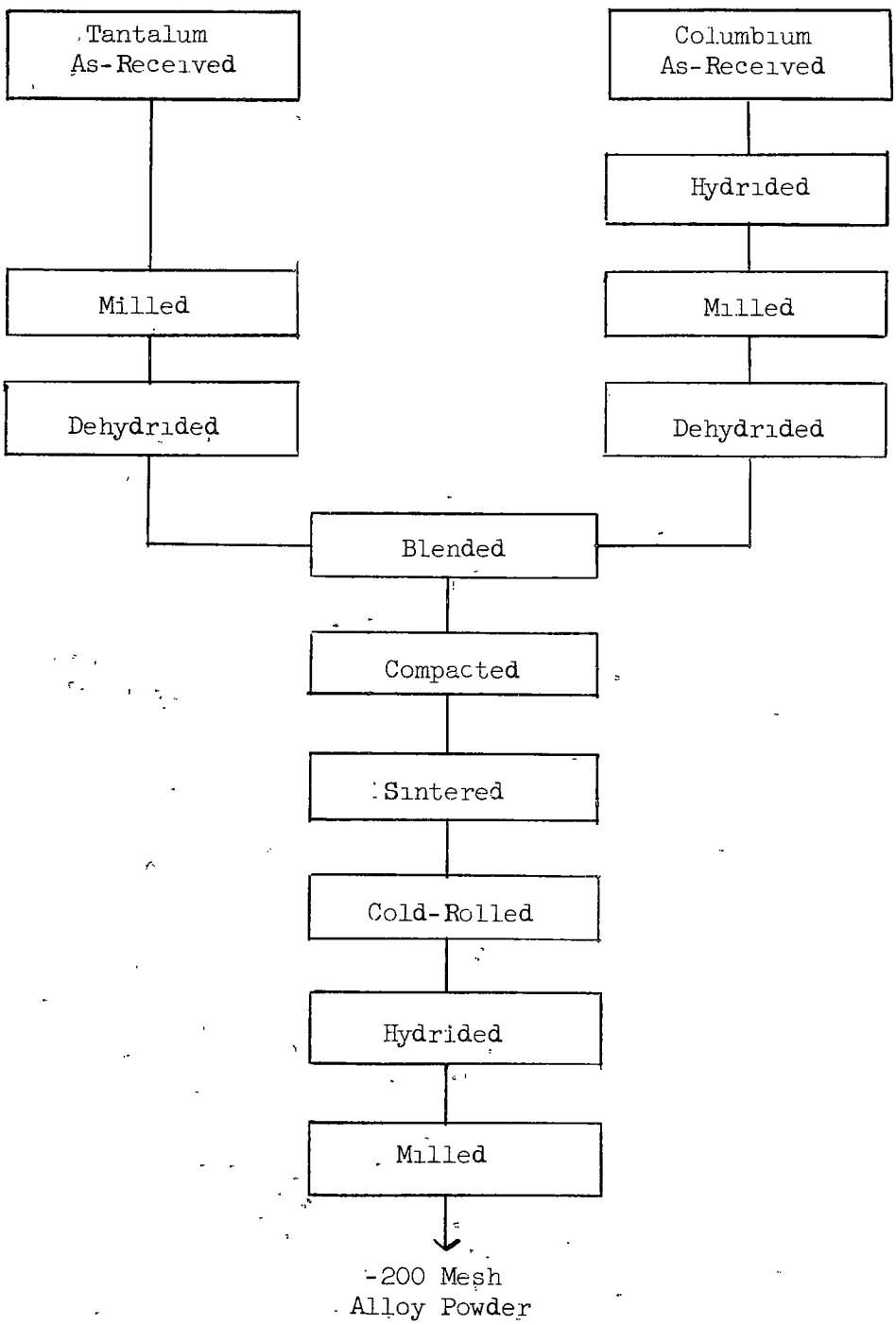

FIGURE 3 - Flowsheet for Production Alloys

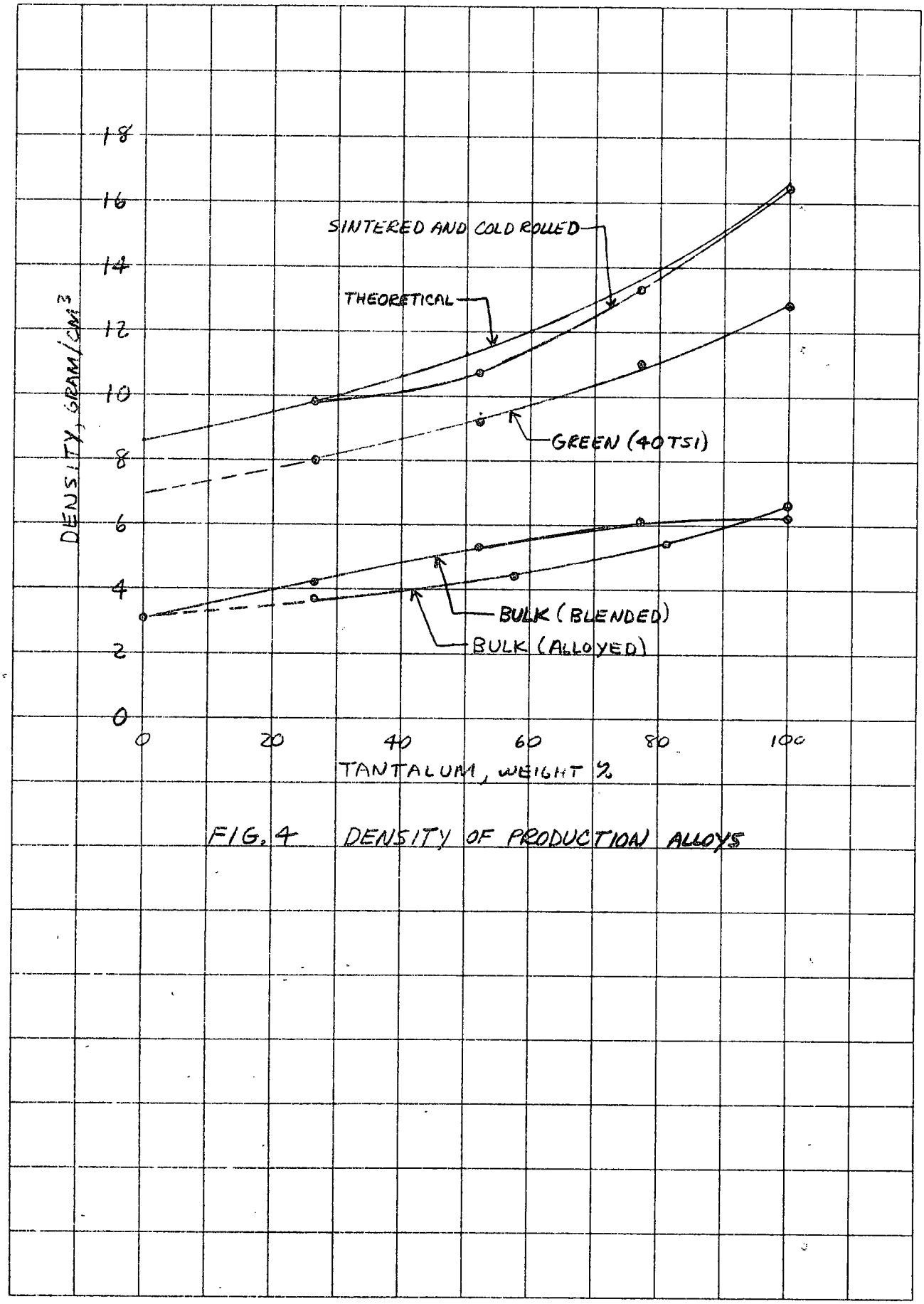

FIG. 4 DENSITY OF PRODUCTION ALLOYS

NO 4520 L 20X20 TO THE INCH

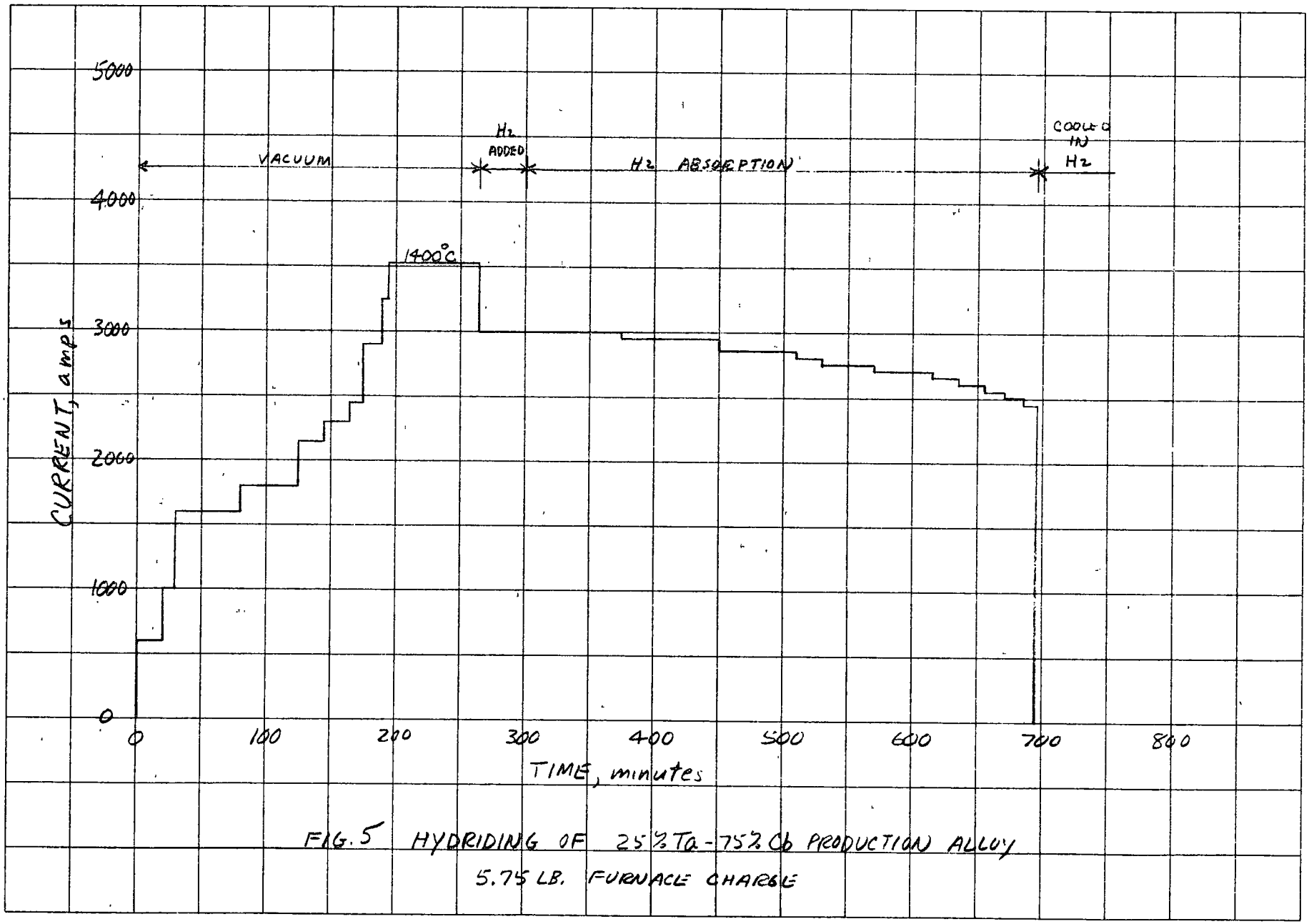

FIG. 5 HYDRIDING OF 25% Ta - 75% Cb PRODUCTION ALLOY
5.75 LB. FURNACE CHARGE

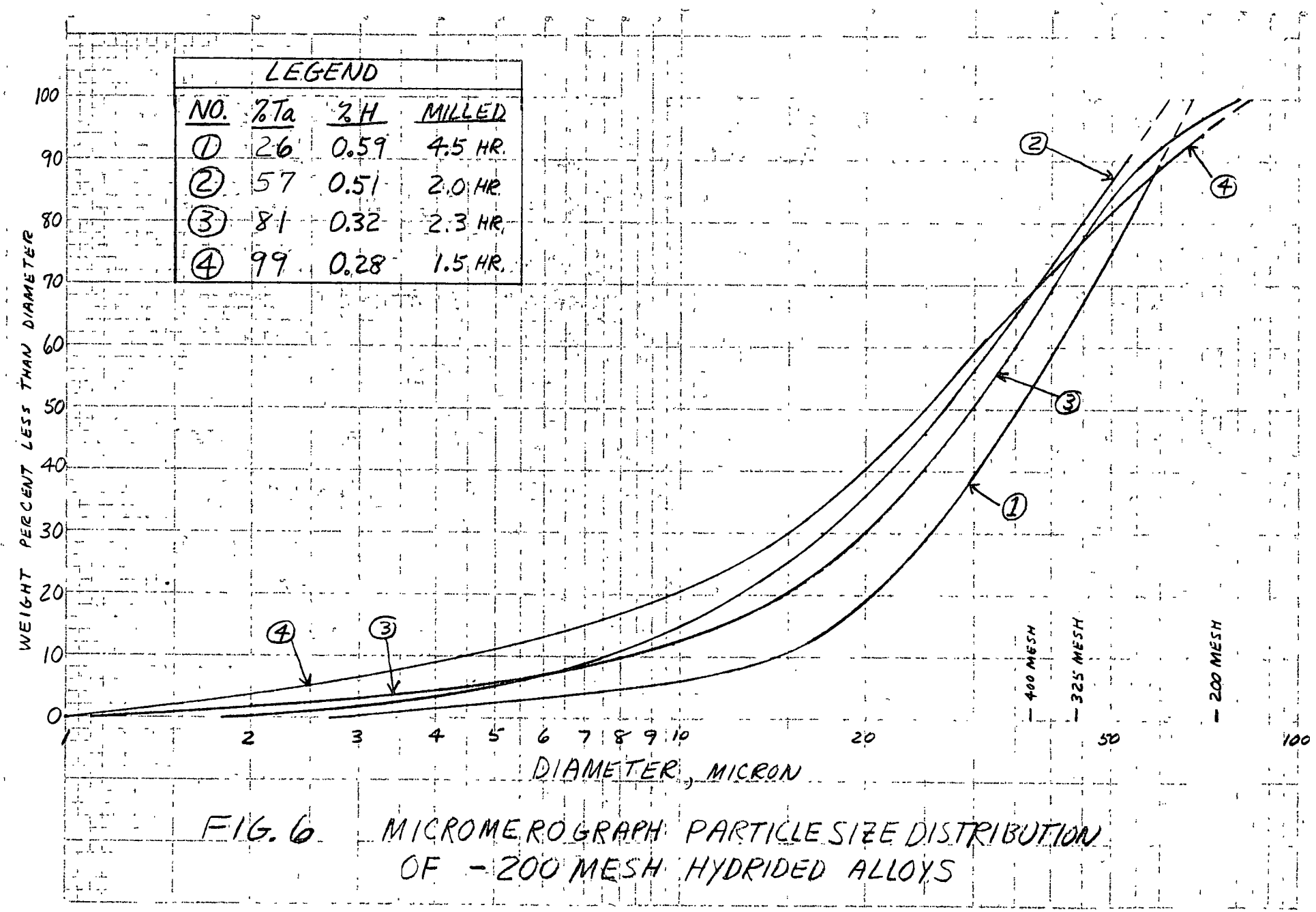

FIG. 6 MICROMEROGRAPH PARTICLE SIZE DISTRIBUTION OF -200 MESH HYDRIDED ALLOYS

APPENDIX

Calculation of Interdiffusion Coefficients

The temperature dependence of the self-diffusion coefficients of tantalum and columbium is as follows:

$$D_{Ta} = 2 \exp. \left[-110{,}000/RT\right] \qquad (2)$$

$$D_{Cb} = 12.4 \exp. \left[-105{,}000/RT\right] \qquad (3)$$

Darken[4] derived the following expression for the interdiffusion coefficient in binary alloys.

$$\tilde{D} = N_1 D_2 + N_2 D_1$$

where: $\tilde{D}$ = interdiffusion coefficient
N_1 = atom fraction of element 1
D_1 = intrinsic diffusion coefficient of element 1
N_2 = atom fraction of element 2
D_2 = intrinsic diffusion coefficient of element 2

For ideal solutions, the intrinsic diffusion coefficient is equal to the coefficient of self-diffusion as measured by the usual radioactive tracer technique. Thus, with the data available, it is possible to estimate the interdiffusion coefficients for tantalum-columbium binary alloys. The diffusion distance (x) in time (t) can then be calculated from

$$x^2 = 4 \tilde{D} t$$

which is an approximation of Fick's second law.

The calculated diffusivities at 1800, 2000, and 2200°C. are given in Table I-A for alloys containing 25, 50, and 75 weight per cent tantalum. Diffusivity is lowest for the 25% tantalum composition.

The diffusion distance required for homogenization during sintering can be estimated from the powder particle size. For -200 mesh powder, the maximum particle diameter is 7.4×10^{-3} cm. (74 microns). For dissimilar particles in contact, the required interdiffusion distance would be 3.7×10^{-3} cm. (37 microns). For the 25% tantalum alloy, this distance would require about 48 hours at 1800°C., five hours at 2000°C., and less than one hour at 2200°C.

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(2) R. L. Eager and D. B. Langmuir, Phys. Rev. 89 (1953); 911
(3) R. Resnick et al., Sylvania Res. Labs, Report No. SEP-252 (March 30, 1959)
(4) L. S. Darken, Trans. AIME 175 (1948), 175

TABLE I-A

Calculated Diffusivity

Temperature			Diffusivity, $cm.^2/sec.$				
°C.	°K.	$10^4/T(°K)$	Ta	Cb	25 w/o Ta	50 w/o Ta	75 w/o Ta
1800	2073	4.82	5×10^{-12}	1.1×10^{-10}	2.02×10^{-11}	4.01×10^{-11}	6.8×10^{-11}
2000	2273	4.40	5×10^{-11}	1.0×10^{-9}	1.88×10^{-10}	3.68×10^{-10}	6.2×10^{-10}
2200	2473	4.04	3.7×10^{-10}	6.5×10^{-9}	1.26×10^{-9}	2.43×10^{-9}	4.05×10^{-9}

$$\log D_{Ta} = \log 2 - 110{,}000/4.575T = 0.301 - 24{,}050/T$$

$$\log D_{Cb} = \log 12.4 - 105{,}000/4.575T = 1.093 - 22{,}950/T$$

$$\tilde{D} = N_{Ta}D_{Cb} + N_{Cb}D_{Ta}$$

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Building 94

May 10, 1963

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E. A Clapp
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MRL-File (6)

"Preparation of Tantalum-Columbium Alloy Powders," by C R McKinsey,
Job Order No 840-95380-P,
Technical Report No P-63-9,
dated May 10, 1963

The enclosed technical report by C R. McKinsey describes the production of columbium-tantalum alloys for the Kemet Division of the Linde Company, to fill their purchase order No 233-41344, as sub-contractors under contract No NObsr 87478 between Linde-Kemet and the Navy Bureau of Ships.

The alloy powder produced met the Kemet specifications with respect to size and composition However, final nitrogen content was slightly high due to unidentified causes

Seven extra copies of the report are being sent to C. M Brown for transmission to Kemet.

G W Healy

GWH cew
Enc (1)